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(30)Priority

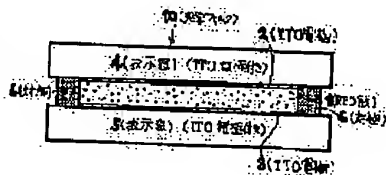
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(54) OPTICAL FILTER

(57)Abstract:

PURPOSE: To obtain a nonlight-emitting type optical filter using a RED material which consumes low electric power and is suitable for a visible ray region by forming such a reversible system that silver from silver salt is precipitated on an electrode or dissolved by driving and controlling electrodes facing to each other.

CONSTITUTION: This optical filter 10 has transparent substrates 4, 5 which constitute a cell as a display window and working electrodes 2, 3 on the inner surfaces of substrates facing to each other. At least one of the electrodes acts as a coloring electrode or color-erasing electrode. counter electrodes 6 are provided to serve also as spacers. A RED liquid 1 containing silver (complex) salt is sealed between electrodes 2, 3. One of the electrodes 2, 3 is used as an anode and the other is used as a cathode. DC driving voltage is applied between these a specified time to cause oxidation-reduction reaction of silver (complex) salt on the cathode side to precipitate Ag. Thus, a transparent state is changed into a colored state. By precipitating Ag on the electrode, a specified color (depending on the silver complex salt used) is observed through the display window and the RED can be used as a filter material.

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26.09.2000

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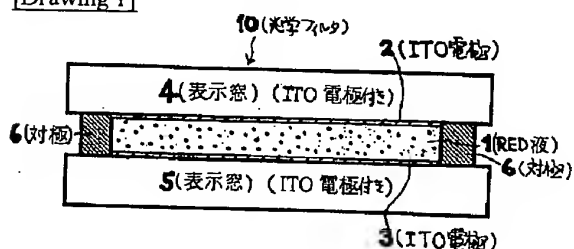
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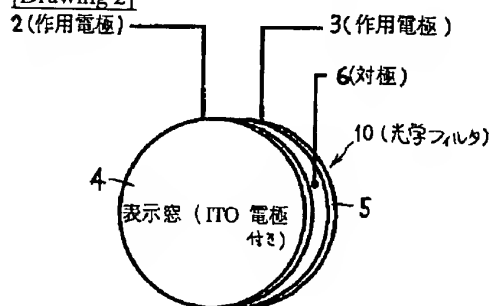
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DRAWINGS

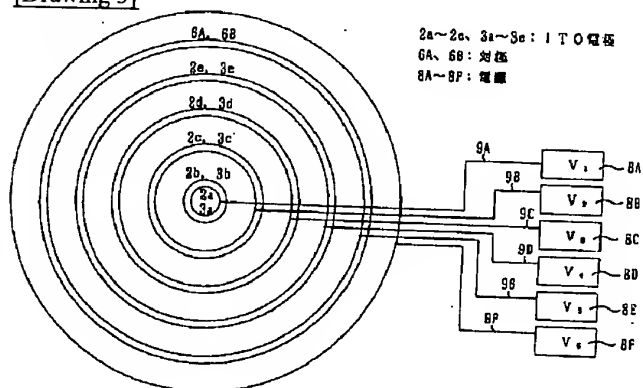
[Drawing 1]



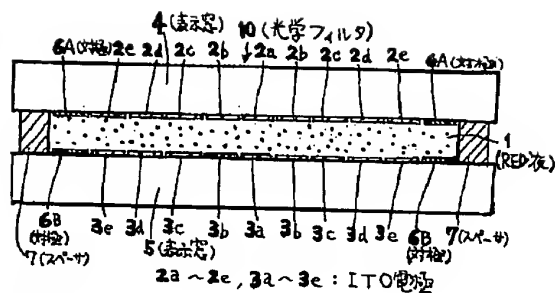
[Drawing 2]



[Drawing 3]



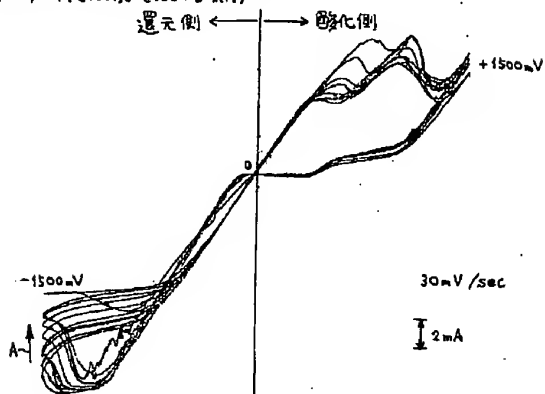
[Drawing 4]



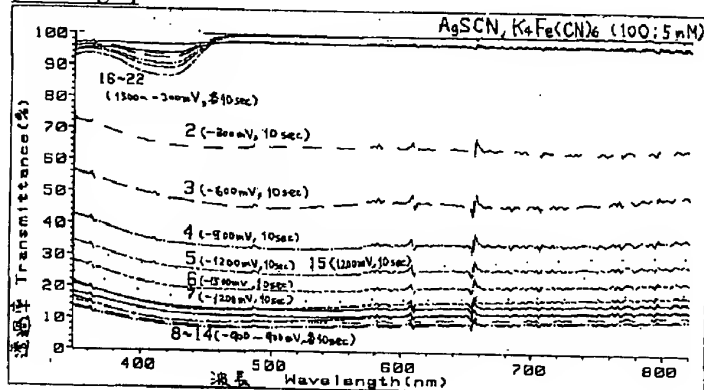
[Drawing 5]

実施例の混合比で作製した溶液のCV曲線

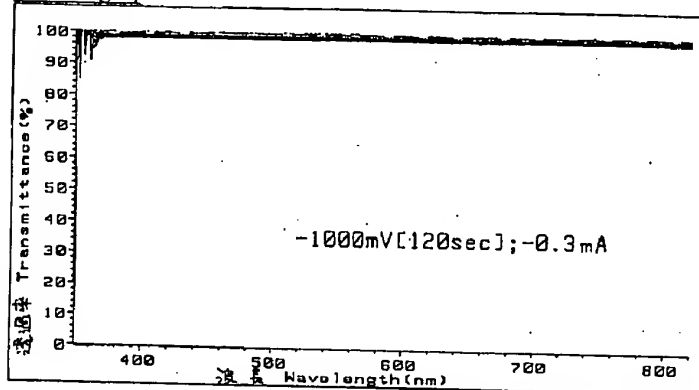
AgSCN , $\text{K}_4\text{Fe}(\text{CN})_6$ (100:5 mM)



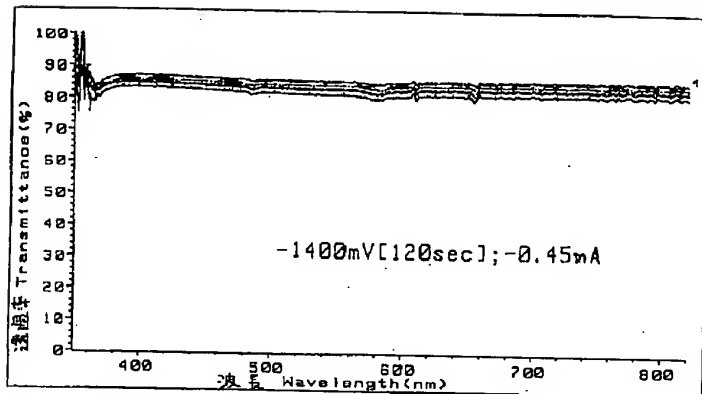
[Drawing 6]



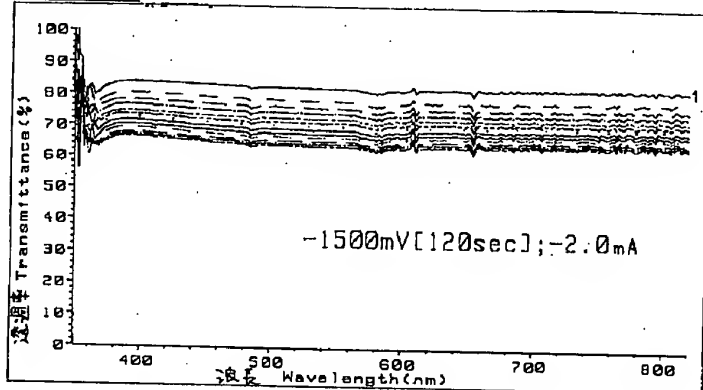
[Drawing 7]



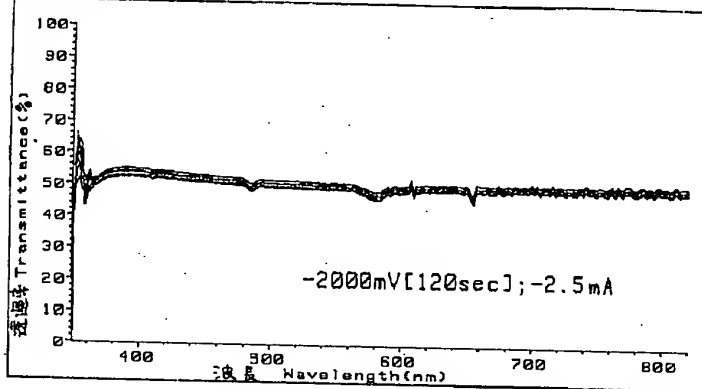
[Drawing 8]



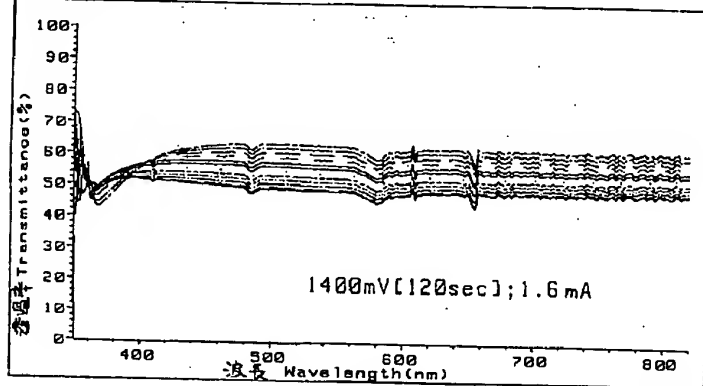
[Drawing 9]



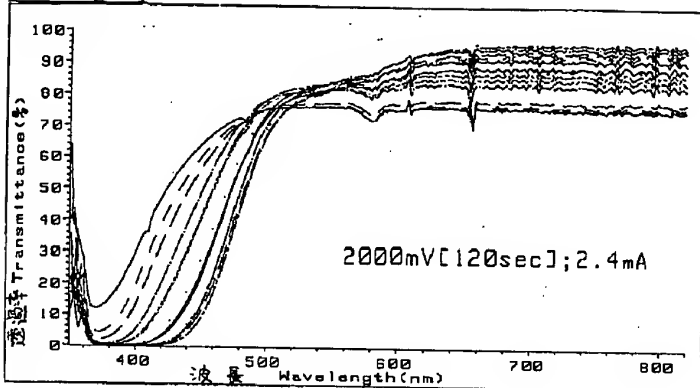
[Drawing 10]



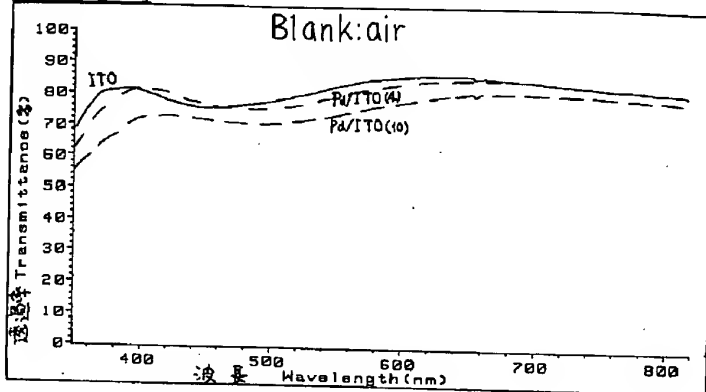
[Drawing 11]



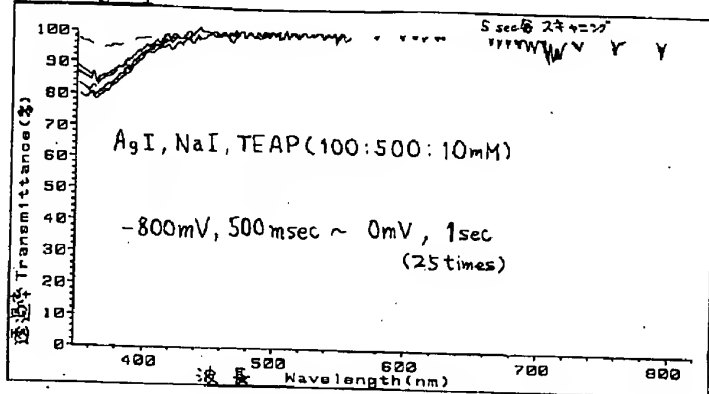
[Drawing 12]



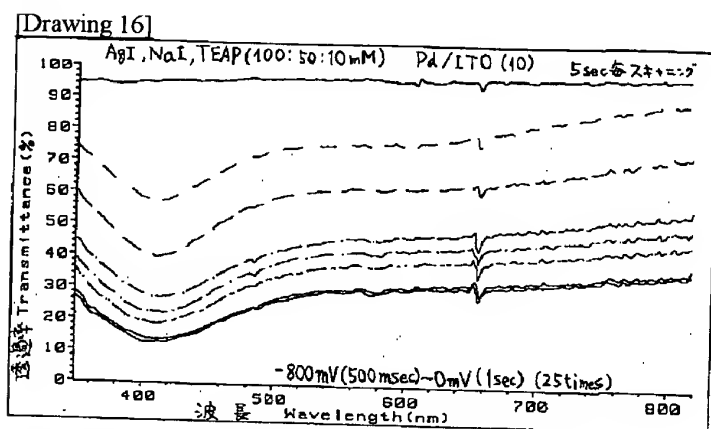
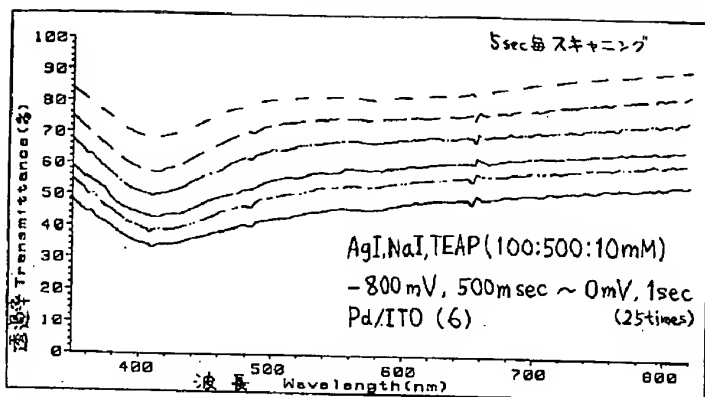
[Drawing 13]



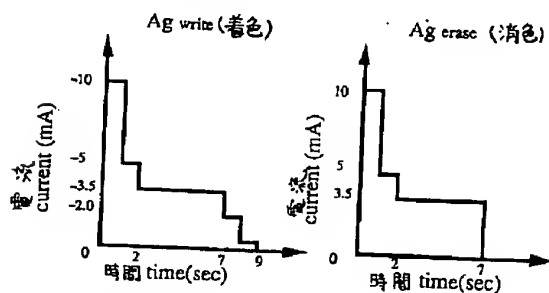
[Drawing 14]



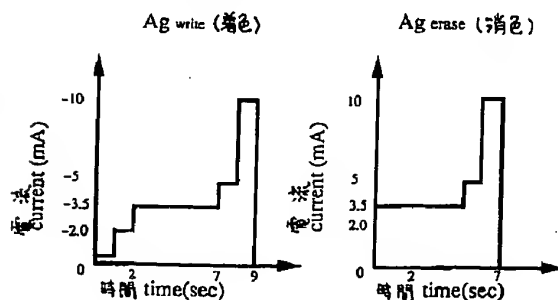
[Drawing 15]



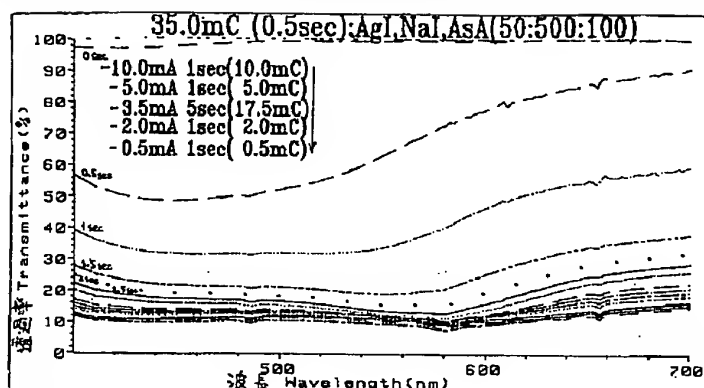
[Drawing 17]
銀の析出溶解のための駆動波形 (高電流値→低電流値)



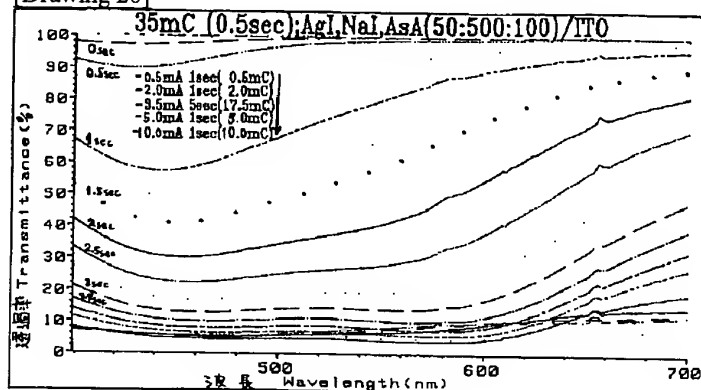
[Drawing 18]
銀の析出溶解に関する駆動波形 (低電流値→高電流値)



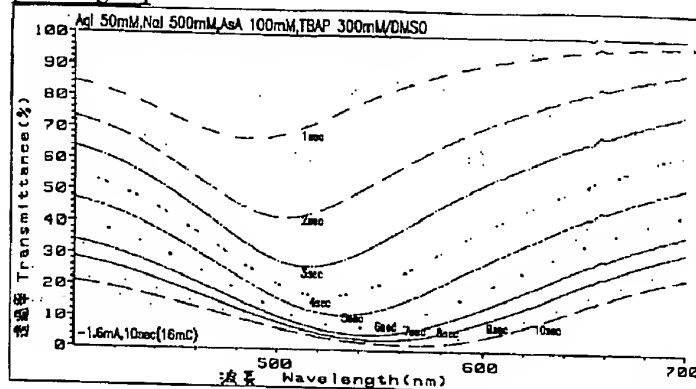
[Drawing 19]



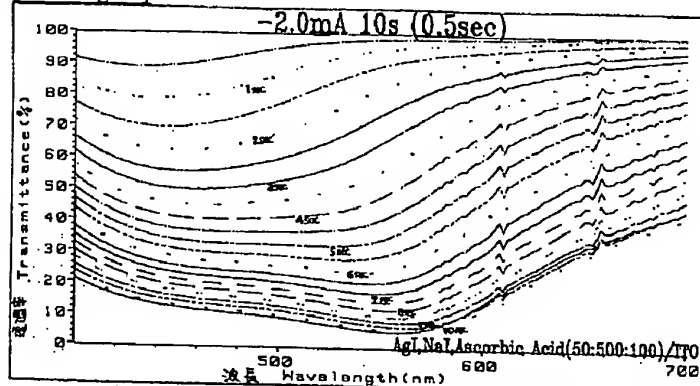
[Drawing 20]



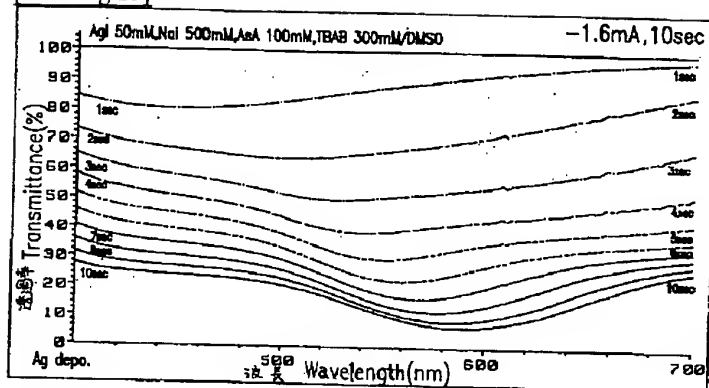
[Drawing 21]



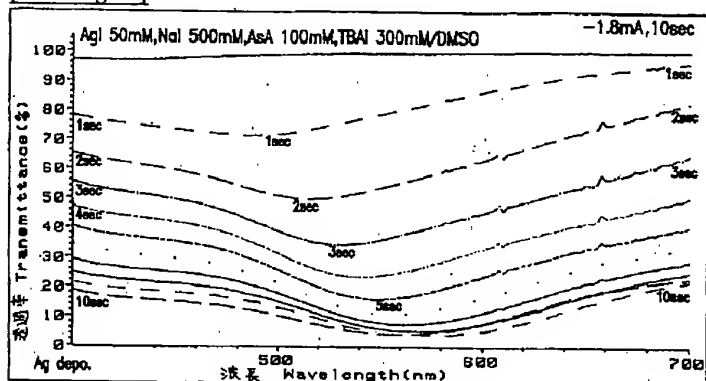
[Drawing 22]



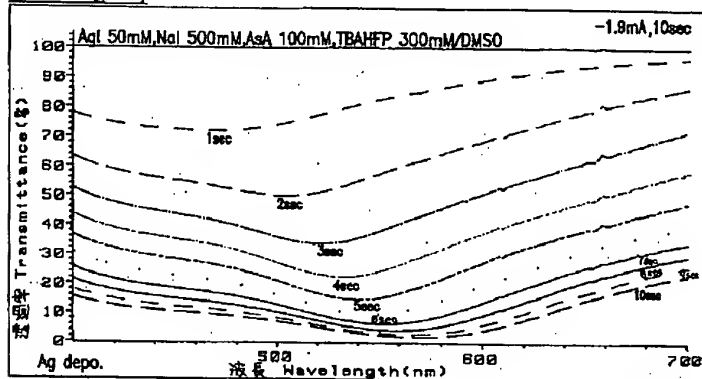
[Drawing 23]



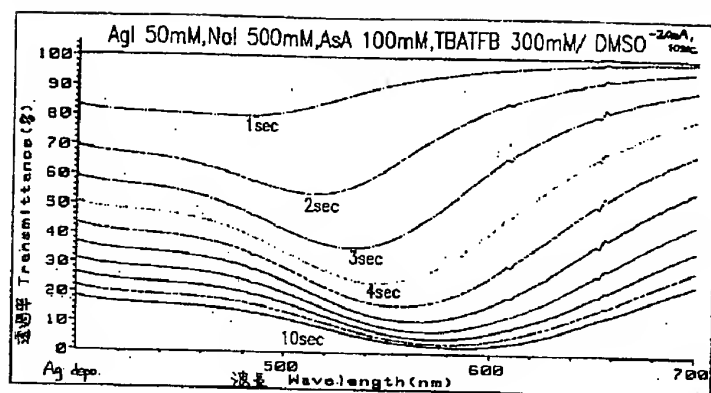
[Drawing 24]



[Drawing 25]



[Drawing 26]



[Translation done.]

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

- [Drawing 1] It is the outline cross section of the light filter by the example of this invention.
- [Drawing 2] It is the conceptual diagram of this light filter.
- [Drawing 3] It is the ITO electrode pattern view of the example of this light filter.
- [Drawing 4] It is the outline cross section of the light filter of this example.
- [Drawing 5] It is valve flow coefficient (cyclic voltammetry) curvilinear view of the RED material used for the example of this invention.
- [Drawing 6] It is the spectrum view showing the permeability change by the applied voltage at the time of coloring of the light filter of this example.
- [Drawing 7] It is the spectrum view showing permeability change of the RED liquid in the specific potential in this example.
- [Drawing 8] It is the spectrum view showing permeability change of the RED liquid in other specific potentials in this example.
- [Drawing 9] It is the spectrum view showing permeability change of the RED liquid in other specific potentials in this example.
- [Drawing 10] It is the spectrum view showing permeability change of the RED liquid in other specific potentials in this example.
- [Drawing 11] It is the spectrum view showing permeability change of the RED liquid in other specific potentials in this example.
- [Drawing 12] It is the spectrum view showing permeability change of the RED liquid in the specific potential of further others in this example.
- [Drawing 13] It is the spectrum view showing permeability change of the electrode when carrying out surface treatment of the electrode in this example.
- [Drawing 14] It is the spectrum view showing permeability change of the RED liquid when carrying out surface treatment of the electrode in this example.
- [Drawing 15] It is the spectrum view showing permeability change of the RED liquid when carrying out surface treatment of the electrode in this example.
- [Drawing 16] It is the spectrum view showing permeability change of the RED liquid when carrying out surface treatment of the electrode in this example.
- [Drawing 17] It is the graph which shows the electrode drive method in this example.
- [Drawing 18] It is the graph which shows other electrode drive methods in this example.
- [Drawing 19] It is the spectrum view showing permeability change of the RED liquid in the drive method of drawing 17.
- [Drawing 20] It is the spectrum view showing permeability change of the RED liquid in the drive method of drawing 18.
- [Drawing 21] It is the spectrum view showing change of the permeability of the RED liquid in the specific potential in this example.
- [Drawing 22] It is the spectrum view showing permeability change of the RED liquid when not adding quarternary ammonium salt in this example.
- [Drawing 23] It is the spectrum view showing change of the permeability of the RED liquid in the specific potential in this example.
- [Drawing 24] It is the spectrum view showing change of the permeability of the RED liquid in the specific potential in this example.
- [Drawing 25] It is the spectrum view showing change of the permeability of the RED liquid in the specific potential in this example.
- [Drawing 26] It is the spectrum view showing change of the permeability of the RED liquid in the specific potential in this example.
- [Description of Notations]
- 1 ... RED liquid (silver salt content liquid)
 - 2, 2a-2e, 3, 3a - 3 e...ITO electrode
 - 4 Five ... Display window (transparent substrate)
 - 6, 6A, 6B ... Counter electrode
 - 7 ... Spacer
 - 8A-8F ... Power supply
 - 10 ... Light filter

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to a light filter.

[0002]

[Description of the Prior Art] Conventionally, electrochromic materials (EC material may be called hereafter) are adopted as the digital clock which is used for voltage drive type display, for example, displays time.

[0003] An electrochromic display device (ECD may be called hereafter) is un-emitting-light type display, and it has an advantage, like driver voltage is comparatively low and there is little power consumption while it has the advantage that there is few feeling of defatigation, also by prolonged observation, since it is the display by the reflected light and the transmitted light. For example, what uses for EC material the viologen molecule derivative of the organic molecule system which forms coloring and a decolorization state in reversible as liquid type ECD is known as indicated by JP,59-24879,A.

[0004] Although the quantity of light regulation device of detailed and a low-power type which replaces an old adjustable ND filter is needed with development of a precision optical instrument, examination with ECD like the above or its circumference technology adapted for it is needed.

[0005] However, since it was satisfied [with obtaining a single color chiefly] of the conventional EC material as an object for display, it was not what meets the above-mentioned demand. And although it was necessary for a light transmittance to be controllable in a light field (wavelength : 400-700nm) as a quantity of light regulation device, old EC material was not enough.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention can be driven by the low power, and is to offer the light filter which can control a light transmittance in a light region.

[0007]

[Means for Solving the Problem] That is, the solution in which silver salt was dissolved is arranged in contact with these electrodes between counterelectrodes, and this invention produces a deposit or the dissolution of silver by drive control of these electrodes, and relates to the light filter constituted so that it might color or decolorize by this.

[0008] According to this invention, when a solution is created, the solution does not have absorption in a light region (wavelength : 400-700nm), and the silver (**) salt in which almost equal cover is possible is used as a material in the light region at the time of coloring. And this silver (**) salt is rich in the reversibility of the deposit-dissolution with drive control. However, such a silver (**) salt has large deposition potential to remarkable negative compared with EC material of an organic system, and it is necessary to make it not damage a transparent electrode without applying potential to a reduction side greatly.

[0009] Thus, especially this invention can offer the light filter suitable at a low power for an un-emitting-light type light region by using the reversible system which it sets [system] to a non-drainage system, and deposits and dissolves silver on a transparent electrode from a silver (**) salt.

[0010] As a silver (**) salt usable to this invention, it is desirable, and the thiocyanogen-ized silver (AgSCN) or the silver halide (AgX:X is the halogen atom) which is rich in reversibility can dissolve this in water or a non-aqueous solvent, and can allot between counterelectrodes as RED (Reversible Electrodeposition) material content liquid (RED liquid is called hereafter.).

[0011] In this case, if a saturation thiocyanogen-ized potassium is used in case thiocyanogen-ized silver is used, the dissolution to the pure water of silver salt can be made easy.

[0012] The concentration of thiocyanogen-ized silver It is good that the RED liquid of the drainage system which is 0.050 - 1.0 mol/L is used.

[0013] When thiocyanogen-ized silver is used, in order to raise a deposit of the silver from the solution, and the reversibility of the dissolution, it is good that a potassium ferrocyanide is added as an auxiliary redox system. Concentration of a potassium ferrocyanide It is good that it is 0.005 - 0.010 mol/L.

[0014] In addition, although cyano ** solutions, such as AgCN used as a plating bath, are conventionally known well about the deposit of the silver from silver complex salt, with a cyano ** solution, there are reservation of a safe work environment and a problem of processing of the waste fluid. Then, it is desirable to use the silver salt of a non-cyanogen system in this invention, and to use AgSCN more stable than especially AgX and AgCN.

[0015] Moreover, as a solvent for dissolving a silver halide, it is good to use a non-aqueous solvent (especially organic solvents, such as an acetonitrile, dimethyl sulfoxide, and a methanol).

[0016] The concentration of a silver halide It is desirable to use the RED liquid of the non-aqueous-solvent system which is 0.005 - 2.0 mol/L.

[0017] Moreover, by embellishing chemically or physically the transparent electrode (especially ITO electrode : thing which doped tin to indium oxide and was obtained.) used as the working electrode which carries out the deposit dissolution of the silver for operating as filter material, the deposition potential of the silver to a transparent electrode can be lowered, the deposit dissolution of silver can be made easy, and the injury which a transparent electrode and the solution itself receive electrically can be mitigated.

[0018] It is good that surface treatment of an ITO electrode is performed as a chemical modification method in this case by the palladium by the 2 liquid approach of a tin solution and a palladium solution. That is, the activity on an ITO electrode front face is raised by depositing a palladium nucleus on an ITO independent substrate as surface activity-ized processing of the ITO electrode by palladium.

[0019] In this case, as a tin solution, it is tin chloride (SnCl_2) 0.10-1.0g. As what was dissolved in HCl [0.010 - 0.10% of] 1L, and a palladium solution, they are palladium chlorides (PdCl_2) 0.10-1.0g. What was dissolved in HCl [0.010 - 0.10% of] 1L is usable.

[0020] Moreover, the method of carrying out the vacuum evaporation of the **** metal from silver to up to an ITO electrode as a physical embellishing method is employable.

[0021] When especially the above-mentioned silver halide is a silver iodide which is rich in reversibility, in order to raise the conductivity of RED liquid, it is good that supporting electrolytes, such as a sodium iodide (NaI), are added by the solution in the range of concentration the isoconcentration of a silver iodide - 20 times.

[0022] In this invention, although the silver (**) salt in which almost equal cover is possible is used as a RED material in a light field, in the deposit from a silver (**) salt, and the dissolution, a solution system is made muddy and it may be hard to maintain the transparency of a solution with the by-product produced when silver dissolves from a deposit electrode.

[0023] It became clear that the iodine generated in case deposit silver is dissolved, when examination is added about this problem, and a silver (**) salt is used as a RED material may make a solution muddy. Then, in order to solve the trouble, muddiness-ization of a solution was able to be prevented by adding the reducing agent which returns deposit iodine to an ionic state.

[0024] Therefore, it is desirable to use the solution which was made to dissolve a silver halide and added the reducing agent as RED liquid in this invention.

[0025] In the system which added the sodium iodide further especially using the silver iodide, in order to suppress a deposit of the iodine generated at the time of the dissolution of deposit silver, and to prevent decline in the permeability of RED liquid and to suppress change of the bath composition by iodine generating, it is good to use an ascorbic acid and/or tin chloride as a reducing agent. In this case, as for a reducing agent, it is desirable to be added in the range of concentration the isoconcentration of a silver halide - 20 times.

[0026] Furthermore, in order to gather conductivity (an electrochemical deposit or the dissolution of silver is carried out smoothly), quantity of electricity which adds quarternary ammonium salt as a supporting electrolyte, consequently a deposit of silver takes can be dropped. Mitigation of quantity of electricity softens the injury on a deposit electrode, and brings a result which raises reliability. In this case, as for quarternary ammonium salt, it is desirable to be added in the range of concentration the isoconcentration of a silver halide - 20 times.

[0027] In this case, it is desirable that it is the basis chosen from the group which the alkyl group of quarternary ammonium salt being a butyl and the anion machine of a supporting electrolyte become from a par chlorate (ClO_4) machine, a bromine (Br) machine, an iodine (I) machine, a hexafluoro phosphate (PF_6) machine, and a tetrafluoroborate (BF_4) machine.

[0028] In the light filter of this invention, in order to operate the substrate electrode for that a solution does not have absorption in a light field in a decolorization state and coloring, and decolorization as a light filter, it is desirable to use an ITO electrode without absorption for a light field.

[0029] And when repeating coloring and a decolorization state using RED liquid, a device cannot stir a solution system to eye a minute hatchet. Then, it is good that quantification of the electrochemical deposit dissolution of silver drives by easy current control.

[0030] As a method of driving the coloring-decolorization by such current control, in order to gather coloring-decolorization speed (a deposit of silver, dissolution rate), it is good to use the driving method by the current which changes from high current value to a low-current value at a rectangle. Or in order to make the injury on the substrate by repeating a deposit of silver and the dissolution mitigate, it is also good to use the driving method by the current which changes from a low-current value to high current value at a rectangle.

[0031]

[Example] Hereafter, the example of this invention is explained.

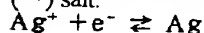
[0032] Drawing 1 and drawing 2 show roughly the light filter 10 by the example of this invention.

[0033] According to the light filter 10 of this example, the transparent substrates (for example, glass plate) 4 and 5 of the couple which constitutes a cell keep a fixed interval, and are arranged as a display window, and the working electrodes (for example, ITO electrode) 2 and 3 from which at least one side serves as an electrode for coloring or an electrode for decolorization counter, and are prepared in the inside of each substrate.

[0034] Moreover, a counter electrode 6 is formed in the perimeter of substrates 4 and 5 to serve also as a spacer, for example, an

argentic plate is used. In addition, although the illustration ellipsis was carried out, the silver wire is prepared as a reference electrode.

[0035] And between counterelectrodes 2-3, the RED liquid 1 which contains the silver (**) salt as a RED material in contact with these electrodes is enclosed. When either of the counterelectrodes 2 and 3 is used as an anode plate, another side is used as cathode and only a predetermined time impresses the driver voltage of a direct current among them, it is [Formula 1] to a silver (**) salt.



The becoming oxidation-reduction reaction is produced in a cathode side, and it is made to shift to a transparence -> coloring state by Ag sludge.

[0036] In this way, by depositing Ag on an electrode, the specific color (it changes with silver complex salt.) by Ag sludge can be observed, and it becomes filter material from a display window. And the filter operation by this coloring, i.e., the permeability of the light, (or shade of coloring) can change with the size or its impression time of voltage, and it can be operated as a permeability adjustable filter by controlling this.

[0037] Although you may have counterelectrodes 2 and 3 all over the simultaneously in a cell, this light filter 10 can be constituted in fact, as shown in drawing 3 and drawing 4.

[0038] That is, the counterelectrode of ITO prepared in the transparent substrates 4 and 5 is divided into Cores 2a and 3a and the ring-like electrodes 2b, 3b, 2c, 3c, 2d, 3d, 2e, and 3e which kept the minute interval in the surroundings of this and were allotted in the shape of a concentric circle, respectively. The counter electrodes 6A and 6B of the silver for potential compensation are formed in the circumference of the counterelectrodes 2e and 3e of the outermost periphery.

[0039] Each of these electrodes 2a, 3a, 2b, 3b, 2c, 3c, 2d, 3d, 2e, 3e, 6A, and 6B are connected to each drive power supplies 8A, 8B, 8C, 8D, 8E, and 8F by the wiring 9A, 9B, 9C, 9D, 9E, and 9F which consists of a chromium thin line etc., respectively.

[0040] And the transparent substrate 4-5 is arranged at predetermined interval by the spacer 7 (the counter electrode 6 serves as this by drawing 1), and RED liquid 1 is enclosed in the interval.

[0041] RED liquid 1 responds to the size of the voltage impressed. An oxidation-reduction reaction Voltage impressed between each above-mentioned division electrode 2a-3a, among 2b-3b, among 2c-3c, between 2d-3d, and among 2e-3e since (namely, concentration) is controlled (it is referred to as V1, V2, V3, V4, and V5, respectively.) The amount of deposits of the silver from the RED liquid on the cathode of each division electrode can be changed (in addition, the voltage V6 for potential compensation is impressed also among counter electrode 6A-6B).

[0042] Therefore, if all voltage is made equal ($V1 = V2 = V3 = V4 = V5$), it can continue throughout RED liquid 1, and can be made to be able to color uniformly, and the grade of concentration can be uniformly changed according to voltage.

[0043] Moreover, coloring concentration serves as size as the applied voltage to each electrode is changed, for example, it goes to the circumference from $V1 < V2 < V3 < V4 < V5$, then a core (if it puts in another way, permeability will serve as smallness). This is useful as optical drawing for CCD (charge-coupled device), such as a television camera, etc., and can fully respond to improvement in the degree of integration of CCD. If applied voltage is made into order contrary to the above, it will apply on the outskirts from a core, and permeability will serve as size.

[0044] Thus, with the applied voltage to a division electrode, a shade or gradation nature can be controlled by various patterns, it becomes useful as a light filter, and the range of the busy condition becomes large.

[0045] According to this example, as explained above, based on a completely different idea from the conventional EC material, the RED material which consists of silver salt was used as filter material for quantity of light regulation of an optical instrument, and the shade at the time of coloring of RED material could be changed by drive control (especially applied voltage) of a counterelectrode, this feature was used, and it became possible to attach gradation to a light filter. Therefore, by use of RED material, it is detailed, and there can be little power consumption, and can end and the filter beyond the capacity of the conventional adjustable ND filter which was operating the mechanical can be offered as a quantity of light regulation device.

[0046] Next, this example is explained in more detail about an example. The light filter which consisted of the following examples like the example shown in drawing 1 and drawing 2 was used.

[0047] Example 1 (use of thiocyanogen-ized silver AgSCN)

It is known that thiocyanogen-ized silver can be dissolved into pure water by existence of the superfluous thiocyanogen ion in a solution. Then, a deposit of silver and mol concentration of thiocyanogen-ized silver desirable to the dissolution It set up with 100 mmol/L and was made to dissolve in a saturation thiocyanogen-ized potassium simultaneously. Simultaneously with it, 5 mmol/L dissolution of the potassium ferrocyanide was carried out as an auxiliary redox system.

[0048] In this way, cyclic-voltammetry measurement (valve flow coefficient measurement is called hereafter.) was performed using the obtained RED solution by -1500mV - +1500mV and trace-speed 30 mV/sec. In valve flow coefficient measurement, the silver wire was used for the ITO electrode and the reference electrode, and the argentic plate was used for the counter electrode on the operation pole. The measurement result was shown in drawing 5.

[0049] Simultaneously with this valve flow coefficient measurement, the trace of change of permeability was also performed. Although the result was shown in drawing 6, permeability was measured every 10 seconds simultaneously with the start of the sweep of the potential of valve flow coefficient measurement. The suffix character of a graph shows the turn of data capture, and corresponds to the data number of the next table 1.

[0050]

表 1

データナンバー	電位 (mV)	データナンバー	電位 (mV)
1	0	13	600
2	-300	14	900
3	-600	15	1200
4	-900	16	1500
5	-1200	17	1200
6	-1500	18	900
7	-1200	19	600
8	-900	20	300
9	-600	21	0
10	-300	22	-300
11	0		
12	300		

[0051] According to the data of drawing 6 the result of the above-mentioned measurement, it turns out that the deposit of Ag advances and permeability falls on cathode with voltage impression, and cover nature continues throughout a light region (400-700nm), and becomes enough. And if polarity of voltage is made reverse, permeability will rise by the dissolution of deposit silver.

[0052] In addition, although it seems that a deposit of silver and the dissolution are rich in reversibility from change of such permeability, by the repeat of a cycle, as Arrow A especially shows by the reduction side, the value has shifted from the result of valve flow coefficient measurement of drawing 5 in the direction which becomes small negative, and it turns out that the deposit of silver and the reaction of the dissolution are progressing in the irreversible direction by the repeat. Moreover, the silver in this example wore, control of the cover nature by decolorization was good, and coloring of a deposit silver film was white.

[0053] Example 2 (use of a silver halide AgX)

The silver halide was used for a deposit of reversible silver and examination of the system of the dissolution. In this example, the silver iodide (AgI) which is rich in reversibility also in a silver (**) salt was used.

[0054] In this example, in order to know silver deposition potential, change of the permeability in various constant potentials was investigated. The acetonitrile of a non-drainage system was used as a solvent. Silver-iodide concentration is made into 1.0 mol/L, it is the purpose which gathers dissolving this and conductivity, and the 1.0 mol/L dissolution of the sodium iodide (NaI) was carried out. This solution was used as RED liquid.

[0055] The trace of change of permeability was performed on the following potential conditions (**-**). Here, the silver wire was used for the ITO electrode and the reference pole, and the argentic plate was used for the working electrode at the counter electrode.

[0056] ** The voltage impression time of -1000mV ** -1400mV ** -1500mV ** -2000mV ** 1400mV ** 2000mV** - ** is all. It is carrying out in 120 seconds and measured continuously in a series of order.

[0057] A result is shown in drawing 7 - drawing 12. The obtained data are the value incorporated every 10 seconds. In the deposit of silver, when potential was -1500mV, a big change appeared as change of permeability. It seemed that change of big permeability was not seen but had contributed to disassembly of a solvent etc. rather in impression of the reduction potential beyond this.

[0058] Moreover, it is 400nm although there is change of permeability considered to be based on the dissolution of a deposit silver film from +1400mV in an oxidization side. It is thought that absorption started in the nearby wavelength field and the deposit of iodine (I₂) started. Moreover, the solution was muddiness-ized with a lot of iodine generating by the superfluous oxidation potential (at the time of +2000mV).

[0059] Example 3 (palladium nucleus surface treatment method)

In order to perform palladium nucleus surface treatment, two kinds of solutions, a palladium solution and a tin solution, were prepared. The manufacture conditions of each solution were as follows.

[0060] a) As a palladium solution palladium solution, it is a 0.1 g palladium chloride (PdCl_2). What was dissolved into 0.1% HCl was used. PdCl_2 Although it began and changed into the distributed state, by stirring for 6 hours, it dissolved and the solution was muddiness-ized.

[0061] b) As a tin solution tin solution, it is SnCl_2 . 0.1 g 0.1% HCl What was dissolved into 100mL was used.

[0062] Next, the electroless-plating method of the ITO electrode using these solutions was as follows.

(1) The tin nucleus was deposited on the ITO electrode (substrate) for 1 minute in the tin solution, stirring.

(2) In order to remove a superfluous tin solution, pure water washed the substrate for 30 seconds.

(3) The tin nucleus which deposited by (1) was made to replace by the palladium nucleus for 1 minute in a palladium solution, stirring.

(4) The superfluous palladium solution was removed by washing for 30 seconds with pure water. More than (1) - (4) A series of work was done 1 cycle.

[0063] Example 4 (change of the permeability of an ITO electrode which performed palladium processing)

In order to investigate the degree of decline in the permeability of the palladium processing ITO electrode produced in Example 3, the permeability of the ITO electrode which carried out palladium processing with the various numbers of cycles was measured.

[0064] Change of the permeability is shown in drawing 13. in this graph, air is taken blank -- 350-820nm up to -- the permeability in a wavelength field is measured The ITO substrate which has not performed palladium processing, and the thing which cycle [a four cycle [Pd (4)] and / 10] [Pd (10)] Repeated palladium processing were used for the sample with which measurement was presented.

[0065] Consequently, it is related with Pd (10) and is abbreviation. 350-650nm It compares with an ITO independent film between wavelength fields, and they are about about 10% and abbreviation. 680-820nm Between wavelength fields, there was decline in about about 5% of permeability. On the other hand, at the thing of Pd (4), there were no unsettled ITO substrate and unsettled great difference.

[0066] Example 5 (measurement of the permeability change using the ITO electrode which performed palladium processing)

An acetonitrile is used for the RED liquid used for this measurement as a solvent, and it is AgI . 100mM, NaI 500mM and tetraethylammonium par chlorate (Tetraethylammoniumperchlorate) (TEAP is called hereafter.) 10mM were dissolved. Using ITO, Pd (6), and Pd (10), the silver wire was used for the reference electrode and the working electrode used the argentic plate for the counter electrode. In addition, the electrochemical cell used for this example was shown in drawing 1.

[0067] Moreover, rectangle applied voltage was used for the driving method. The used method of driving rectangle applied voltage (vs. Ag wire) was as follows (the inside of a parenthesis is the holding time).

- 800MV(500Msec)0 MV (1Sec) [0068] The permeability by Ag film which deposited on the working electrode was repeatedly measured using this rectangle applied voltage 25 times. Moreover, the permeability of the ITO substrate before carrying out electrocrystallization was used for the blank at this time. The result is shown below.

[0069] The thing when using Pd (10) for drawing 15 for the thing when using Pd (6) for drawing 14 for change of the permeability when using an ITO independent substrate as a working electrode as a working electrode as a working electrode is shown in drawing 16, respectively. It was measuring about the graph of change of each permeability, and the 350-800nm wavelength field, and data were gained every 5 seconds.

[0070] consequently, ITO -- an independent thing -- the said driving method -- setting -- wavelength what performed palladium processing to about 2% of cover having been near 460nm -800mV ** -- it says -- comparatively, by the electrocrystallization in a low battery, there is it by Pd (6), there is 68 - 84% of cover by Pd (10) 45 to 65%, and the working electrode at the time of the maximum cover was presenting thin black

[0071] The deposit gestalt of Ag was able to change with the nuclei of the palladium which adhered on ITO from the above result a lot, and the potential for depositing Ag was able to be brought considerably close to the potential of a reference electrode. Power consumption which the drive when mitigating the injury on the working electrode by overvoltage impression, and using as a RED material by this takes can be made small.

[0072] Example 6 (high current-value -> drive to a low-current value)

It is a sodium iodide about silver-iodide 50mM in dimethyl sulfoxide (DMSO). It is made to dissolve with 500mM and is an ascorbic acid (AsA) as a reducing agent. What carried out the 100mM dissolution was used as RED liquid. It was filled up with RED liquid into the electrochemical cell for which the working electrode (ITO electrode used as the substrate for the deposit-dissolution of silver), the counter electrode (argentic plate), and the reference electrode (silver wire) were prepared, and measurement was presented.

[0073] Before measuring, the potentiostat was used, valve flow coefficient (cyclic voltammetry) measurement was performed, and quantity of electricity required in order to obtain the deposit-lytic reaction of reversible silver was estimated. Consequently, it was estimated as about 41.7 mC/cm² and 38.7 mC/cm², respectively. A deposit and the dissolution of the silver from the RED solution by current control were tried using the galvanostat using this quantity of electricity. The following method was adopted about the drive method of the current value at that time.

[0074] That is, a deposit of the silver by the constant current and the dissolution are shifted from high current to a low current, and are performed, and what is shown in the following Table 2 and 3 (drawing 17) as an example of the driving method can be

considered. Moreover, the time which is made to shift current value by the rectangular step type impressing method, and change of current value takes shall be disregarded.

[0075]

表 2

(銀の析出のための駆動法：高電流値→低電流値)

	電流値(mA)	維持時間(sec)	電気量(mC)
1)	-10.0	1.0	10.0
2)	-5.0	1.0	5.0
3)	-3.5	5.0	17.5
4)	-2.0	1.0	2.0
5)	-0.5	1.0	0.5

[0076]

表 3

(銀の溶解のための駆動法：高電流値→低電流値)

	電流値(mA)	維持時間(sec)	電気量(mC)
1)	+10.0	1.0	10.0
2)	+5.0	1.0	5.0
3)	+3.5	5.0	17.5

[0077] The graph which pursued change of the permeability is shown in drawing 19 about the cover speed when using this driving method. moreover, acquisition of data 0.5sec every -- it is carrying out and it turns out in about 4 seconds that permeability has reached to 20% or less

[0078] Example 7 (drive to low-current value → quantity current value)

A deposit of the silver by the low current and the dissolution are shifted from a low-current value to high current value, and the step impressing method was used like Example 6. The driving method shown in the following Table 4 and 5 (drawing 18) as an example is mentioned.

[0079]

表 4

(銀の析出のための駆動法：低電流値→高電流値)

	電流値(mA)	維持時間(sec)	電気量(mC)
1)	-0.5	1.0	0.5
2)	-2.0	1.0	2.0
3)	-3.5	5.0	17.5
4)	-5.0	1.0	5.0
5)	-10.0	1.0	10.0

[0080]

表5
(銀の溶解のための駆動法：低電流値→高電流値)

	電流値(mA)	維持時間(sec)	電気量(mC)
1)	+3.5	5.0	17.5
2)	+5.0	1.0	5.0
3)	+10.0	1.0	10.0

[0081] The graph of the change of permeability to drawing 20 is shown. Data are gained every 0.5sec(s) like [this graph] drawing 19. Consequently, the last cover was good although cover speed was late from the low-current value by the method of driving high current value compared with the thing (Example 6) of the reverse driving method (attainment time : abbreviation with a permeability of 20% 4.5 - 5.0 second).

[0082] The big difference was found by decline in early permeability although the difference was not looked at so much by the maximum decline in the permeability 9 seconds after using each driving method as a result of examining cover speed and the degree of cover using the method of driving two kinds as mentioned above.

[0083] Furthermore, as a result of observing the gestalt of Ag film which carried out electrocrystallization using this method of driving two kinds with a scanning electron microscope (SEM), it turns out that particle size has gathered compared with the driving method (Example 6) the deposit Ag nucleus when using the method of driving the low-current value -> quantity current value of Example 7 is reverse.

[0084] Example 8 (endurance test)

Using the method of driving two kinds, Example 6 and Example 7, it wore and the preliminary test for checking the endurance about decolorization (a deposit of silver, dissolution) was performed. Consequently, it is abbreviation with the method of driving Example 6. It checked that the repeat of about 1000 or more cycles was possible by 800 cycle and the method of driving Example 7.

[0085] Therefore, in a meaning called drive speed, the method of driving the high current-value -> low-current value of Example 6 is effective, and it turns out that the method of driving the low-current value -> quantity current value of Example 7 is effective in reduction of an electrode dissipation blemish.

[0086] Example 9 (effect of iodine generating suppression of a reducing agent)
Conventionally, when dissolving the silver after a deposit in the reaction like the above, since iodine (I₂) generated like the following formula 1 simultaneously and this made a solution system muddy in blackish brown, it had become a problem.

2I⁻ -> I₂ + 2e⁻ ... (formula 1)
[0087] However, the deposit of I₂ was able to be suppressed by mixing the low reducing agent of a standard oxidation reduction potential in a solution rather than iodine.

[0088] That is, although the ascorbic acid contains in it, the system in which the ascorbic acid was dissolved is colorlessness, and since a solution was not made muddy in the RED solution stated in Example 6, it is advantageous to it for the permeability of a light filter. And since the ascorbic acid acted as a reducing agent and iodine was ionized, the deposit I₂ at the time of dissolving silver could be suppressed, and a solution did not become muddy in I₂. It is thought from this point that an ascorbic acid is the optimal.

[0089] moreover, even if it replaced with the ascorbic acid and used tin chloride (or -- using together), there was the same I₂ deposit prevention operation as the above. However, when adding a reducing agent, although the depressor effect of deposit I₂ is possible at selection of a reducing agent, in order to apply it as a light filter to the last, use of the reducing agent (it does not become the cause of a fall of permeability) which does not make a solution system muddy is desired.

[0090] Example 10 (the addition effect of quarternary ammonium salt)
When performing a deposit of silver and the dissolution using above-mentioned RED liquid, mixing of quarternary ammonium salt was tried in order to raise the conductivity of RED liquid. It is a tetrabutyl ammonium par chlorate (Tetrabutylammoniumperchlorate) to the RED liquid used in Example 6 (TBAP). What carried out 300mM addition shows the graph of change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 16mC(s)) to drawing 21 for 10 seconds by 1.6 mA. moreover, the RED liquid which does not add quarternary ammonium salt with this RED liquid is used for drawing 22 -- 2.0 mA shows the graph of change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 20mC(s)) for 10 seconds

[0091] The current value which decline in permeability takes was able to be reduced by adding quarternary ammonium salt as a supporting electrolyte so that these results might show. It is possible that the overvoltage concerning an electrode can be made to mitigate and the number of times of a repeat of the deposit dissolution may be increased by this (by the deposit dissolution by the spectrum of drawing 21, 2000 times or more of repeats were checked.). Moreover, the permeability at the time of the dissolution of silver is a simultaneously. It was 100%.

[0092] Moreover, as follows, other quarternary ammonium salt was added, change of the permeability obtained like the above

was measured, and the result was shown in drawing 23 - drawing 26.

[0093] Drawing 23: the RED liquid used in Example 6 -- tetrabutyl ammonium star's picture (Tetrabutylammoniumbromide) (TBAB) it is what carried out 300mM addition -- change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 16mC(s)) for 10 seconds by 1.6 mA

[0094] Drawing 24: the RED liquid used in Example 6 -- tetrabutyl ammonium -- I_o -- DAIDO (Tetrabutylammoniumiodide) (TBAI) it is what carried out 300mM addition -- change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 18mC(s)) for 10 seconds by 1.8 mA

[0095] Drawing 25: the RED liquid used in Example 6 -- tetrabutyl ammonium hexafluoro phosphate (Tetrabutylammoniumhexafluorophosphate) (TBAHFP) it is what carried out 300mM addition -- change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 19mC(s)) for 10 seconds by 1.9 mA

[0096] Drawing 26: the RED liquid used in Example 6 -- tetrabutyl ammonium tetrafluoroborate (Tetrabutylammoniumtetrafluoroborate) (TBATFB) it is what carried out 300mM addition -- change of the permeability when trying a deposit of the silver in a constant current (quantity of electricity being 20mC(s)) for 10 seconds by 2.0 mA

[0097] Even if it added the above-mentioned various quaternary ammonium salt as a supporting electrolyte also from these results, the current value which decline in permeability takes was able to be reduced (however, it is thought that they will improve further if the data of drawing 23 show the good result although current is 1.6mA, and they increase current.). It is possible that the overvoltage concerning an electrode can be made to mitigate and the number of times of a repeat of the deposit dissolution may be increased by this.

[0098] As mentioned above, although the example of this invention was explained, an above-mentioned example can deform further based on the technical thought of this invention.

[0099] For example, various the kind of RED material mentioned above, combination of a RED liquid component, concentration, etc. may be changed, and are not restricted to what also illustrated silver salt to ****.

[0100] Moreover, the structure of the light filter containing an ITO electrode pattern is begun, and it is not limited to the quality of the material of each component, and the thing which also mentioned the drive method above further. for example, the ***** pattern shown in drawing 3 can be changed to various like the shape of the stripe, and a grid as filter structure, and the cell of different RED liquid for every division electrode can also be divided and juxtaposed In this case, RED liquid and conventional EC liquid are also combinable.

[0101] Moreover, the light filter by this invention can be combined with other well-known filter material (for example, the electrochromic material of an organic system, liquid crystal, electroluminescence material). Moreover, the light filter by this invention can begin the object for optical drawing of CCD, and can apply it widely also as objects for quantity of light regulation, such as various optical system and also an electrophotography copying machine, and an optical-communication device.

[0102]
[Function and Effect of the Invention] As mentioned above, the light filter by this invention uses the RED liquid containing silver salt as filter material for quantity of light regulation of an optical instrument based on a completely different idea from the conventional EC material, and forms the reversible system which deposits and dissolves the silver by silver salt on an electrode by drive control (especially applied voltage) of a counterelectrode. Therefore, the suitable light filter for an un-emitting-light type light region can be offered by the low power using RED material.

[Translation done.]